

PATENT SPECIFICATION

760.624



Date of Application and filing Complete Specification May 6, 1954.

No. 13294/54.

Application made in Canada on May 9, 1953.

Application made in United States of America on Oct. 22, 1953.

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Index at acceptance: —Classes 1(3), A1D(45:46), A1G13D45, A1G(3:5:6:8:9:11:22:30:39), D(45:46), A1N13A; 82(1), O8F1; and 90, K9B.

COMPLETE SPECIFICATION

Improved method for the Treatment of Mineral Sulphide Ores

ERRATA

SPECIFICATION No. 760,624

Page 1, line 24, for "Sulfide ores" read
"Sulphide ores"
Page 2, line 31, for "atosphere" read
"atmosphere"
Page 2, line 109, for "Pyrrohitite" read
"Pyrrhotite"
Page 3, line 78, for "pellet" read "pellets"
Page 4, line 2, for "phase" read "Phases"
Page 4, line 37, for "received" read
"recovered"
Page 5, lines 29 and 36, for "valves" read
"values"

THE PATENT OFFICE,
3rd September, 1957.

30 effluent combustion gases are treated for the recovery of sulphur dioxide. Prior art methods of recovering sulphur dioxide from roaster and smelter gases are incidental to the recovery of metal values which is the primary objective of such methods, and originally, were designed to separate sulphur dioxide from the combustion gases so that the gases could be released to the atmosphere. However, due to progressively increasing demands for sulphur by industry and the depletion of cheap and readily available sources of elemental sulphur, methods of treating mineral sulphides primarily for the recovery of sulphur values are being closely investigated. For example, a smelting method has been devised by means of which a gas containing up to about 75% sulphur dioxide is produced, from which substantially pure sulphur dioxide can be recovered. Other methods involve roasting pyritic and pyrrhotitic mineral sulphides pri-

75 of ores for separating valuable constituents from gangue material and for selectively concentrating a mineral or a group of minerals as a small fraction of a larger body of starting material which contains values of economically recoverable minerals. 80

There are, however, ores which are not easily or directly amenable to conventional flotation processes. Also, in the operation of a selective flotation process, there usually is produced a middling product which contains small percentages of desired minerals and from which metal values can be recovered only with great difficulty and at high cost. For example, in the selective flotation of lead-zinc ores a middling product is formed which contains values of both metals. Also, in the selective flotation of nickel-copper ores, a middling product is obtained which contains values of both nickel and copper. Such middling products contain relatively small 85 90 95

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COMPLETE SPECIFICATION

Improved method for the Treatment of Mineral Sulphide Ores

We, CHEMICAL CONSTRUCTION CORPORATION, a company incorporated under the laws of the State of Delaware, United States of America, of 488, Madison Avenue, New York City, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of treating pyrrhotitic mineral sulphides for the production of sulphur and for the extraction of such non-ferrous metal values as may be contained in the pyrrhotitic material.

The potential economic value of sulphur contained in mineral sulphide ores and concentrates has long been recognized and various methods for its recovery are well known and are in wide spread use. Existing methods of recovering sulphur values from mineral sulphide ores and concentrates heretofore usually have been associated with the treatment of metal-bearing sulfide ores and concentrates in the concentration of and primarily for the extraction of metal values, such as in oxidizing roasting and smelting operations wherein effluent combustion gases are treated for the recovery of sulphur dioxide. Prior art methods of recovering sulphur dioxide from roaster and smelter gases are incidental to the recovery of metal values which is the primary objective of such methods, and originally, were designed to separate sulphur dioxide from the combustion gases so that the gases could be released to the atmosphere. However, due to progressively increasing demands for sulphur by industry and the depletion of cheap and readily available sources of elemental sulphur, methods of treating mineral sulphides primarily for the recovery of sulphur values are being closely investigated. For example, a smelting method has been devised by means of which a gas containing up to about 75% sulphur dioxide is produced, from which substantially pure sulphur dioxide can be recovered. Other methods involve roasting pyritic and pyrrhotitic mineral sulphides pri-

marily for the recovery of sulphur dioxide.

Prior art methods have the important disadvantage that sulphur dioxide bearing gases recovered from pyrometallurgical operations, such as smelting and oxidizing roasting operations, usually contain dust particles which must be separated from the combustion gases. Also, the sulphur dioxide content usually is relatively low thereby necessitating the installation and operation of costly gas treating equipment. Also, of course, the sulphur content of the starting material is recovered from these processes as sulphur dioxide and the production of elemental sulphur therefrom requires the use of methods and apparatus for reducing the sulphur dioxide to elemental sulphur.

A primary object of this invention is to provide a method for the treatment of pyrrhotitic mineral sulphides for the recovery of elemental sulphur.

Processes for concentrating selected non-ferrous mineral values from other minerals with which they are associated in an ore also are well known and are widely used in the mining industry. The flotation process is probably the most widely used method of wet concentration of ores for separating valuable constituents from gangue material and for selectively concentrating a mineral or a group of minerals as a small fraction of a larger body of starting material which contains values of economically recoverable minerals.

There are, however, ores which are not easily or directly amenable to conventional flotation processes. Also, in the operation of a selective flotation process, there usually is produced a middling product which contains small percentages of desired minerals and from which metal values can be recovered only with great difficulty and at high cost. For example, in the selective flotation of lead-zinc ores a middling product is formed which contains values of both metals. Also, in the selective flotation of nickel-copper ores, a middling product is obtained which contains values of both nickel and copper. Such middling products contain relatively small

amounts of metal values but represent a serious loss of metal values if discarded and high capital and operating costs if treated for the recovery of the metal values.

- 5 A further important object of this invention is to provide a method for the treatment of pyrrhotitic mineral sulphides which contain non-ferrous mineral values for the recovery of elemental sulphur and non-ferrous mineral values.

10 It has been found that, by the process according to this invention, elemental sulphur can be produced from pyrrhotitic mineral sulphide ores and concentrates.

- 15 It is found further that this process of producing elemental sulphur is also ideally adapted for treating pyrrhotitic material which is associated with non-ferrous metal values for the production of elemental sulphur and for the extraction and separation therefrom of non-ferrous metal values.

The term "pyrrhotitic mineral sulphides" is intended to mean any mineral sulphides which contain no labile sulphur or from which the labile sulphur has been removed. Thus the sulphur content may be present in pyrrhotite, an iron sulphide having the general formula FeS .

- Pyritic material, such as pyrite, FeS_2 , can be converted into pyrrhotitic material by heating in an atmosphere free of oxygen or containing less than half the stoichiometric amount of oxygen necessary to convert all sulphide sulphur to sulphur dioxide. This product has the characteristics of pyrrhotite insofar as the sulphur content is concerned and as such is a pyrrhotitic material within the terms of this disclosure and is ideally adapted for treatment by the present method. Other ores or concentrates which contain minerals such as, but not limited to, chalcocite, enargite, tetrahedrite, rennellite, arsenopyrite, pentlandite, cobaltite, marcasite, bornite, famatinite, stannite, millerite, chalcopyrite, and sphalerite can be treated according to the process of this invention, or, if necessary, first treated in a manner similar to that described above with respect to pyrite.

A primary object of this invention is to treat pyrrhotitic mineral sulphides for the production of elemental sulphur. The pyrrhotitic mineral sulphides, therefore, may be barren of economically recoverable non-ferrous metal values.

- The method of producing elemental sulphur from pyrrhotitic mineral sulphides of the present invention comprises, in general, the steps of reacting pyrrhotitic mineral sulphide particles dispersed in an aqueous acidified sulphate solution (as hereinafter defined) or in water containing a small amount of sulphuric acid at a temperature within the range of from 100°F . to 290°F . with a free oxygen bearing gas under a partial pressure of free oxygen above 25 pounds per square inch, containing the reaction to oxidize sulphide sulphur con-

tained in the pyrrhotitic material to elemental sulphur, agglomerating the elemental sulphur to liquid sulphur globules, cooling the liquid sulphur globules below the melting temperature of sulphur to form elemental sulphur pellets, and recovering elemental sulphur pellets from the reaction mixture.

The pyrrhotitic mineral sulphides may be associated with non-ferrous mineral sulphides which add to the potential economic value of the starting material. Such non-ferrous metal values associated with pyrrhotitic material include, for example, values of metals such as copper, zinc, gold, silver, cobalt, nickel and cadmium.

Pyrrhotitic mineral sulphide material to be treated by the method of this invention is finely pulverized. When mixed with an aqueous acidified sulphate solution to form a slurry, a relatively uniform dispersion of particles is obtained to expose maximum surface area of the particles to the free oxygen-bearing gas and the aqueous acidified sulphate solution. While the size of the particles may vary widely, it has been found that the reaction rate and the extraction of sulphur and non-ferrous metal values, if present in the starting material, are best when the starting material is from 35 to 325 mesh Standard Tyler Screen. Pyrrhotitic mineral sulphides received from preliminary concentrating processes such as from flotation cells, may be of from 100 to 325 mesh and can be passed directly into the method of this invention. Material which otherwise has not been reduced in size can be pulverized to 35 mesh or finer.

Sulphuric acid is formed autogenously as the oxidation reaction proceeds, the pH value of the solution remaining relatively constant at about pH 2. The method can be conducted as a batch operation, pyrrhotitic mineral sulphides being dispensed in an aqueous acidic sulphate solution from a previous oxidation treatment of pyrrhotite mineral sulphide which has been acidified with sulphuric acid, referred to herein as an "aqueous acidified sulphate solution", or in water to which a small amount of sulphuric acid has been added. Alternatively, mineral sulphides and water can be charged, continuously or intermittently, into the reaction vessel which contains a slurry of mineral sulphides and aqueous acidified sulphate solution undergoing treatment. Undissolved residue, aqueous acidic sulphate solution, elemental sulphur and, if present, non-ferrous mineral sulphides can be discharged continuously or intermittently from the reaction vessel.

The oxidation of sulphide sulphur contained in the pyrrhotitic material usually provides the heat necessary for the reaction. If this heat is not sufficient, supplemental heat can be provided by any suitable means. If the autogenous heat of the reaction tends to raise the temperature beyond the desired limits, the

temperature can be controlled by conventional means, such as cooling coils.

The pulp density, or the ratio by weight of solids to aqueous acidified sulphate solution, influences the rate of oxidation of the sulphide sulphur to elemental sulphur. The velocity of the reaction is reduced as the pulp density is increased, the maximum pulp density being that at which the solids can be maintained as a relatively uniform dispersion in the solution. The minimum density is governed by operating economics to obtain a maximum yield of sulphur within a reasonable time. Thus, the pulp density can vary within reasonably broad limits. A very satisfactory range is from 35% to 45% solids. This range of densities provides for a rapid rate of oxidation and of relatively rapid dissolution of non-ferrous metal values contained in the starting material.

In the present invention, the oxidation reaction is conducted at temperatures of from 100° F. to 290° F. The best results appear to be obtained within a relatively narrow temperature range of from slightly below to slightly above the melting temperature of sulphur. That is, from 200° F. to 290° F. Within this range, oxidation of sulphide sulphur proceeds rapidly with a high yield of elemental sulphur.

When the oxidation step is conducted at a temperature slightly below the melting point of sulphur, the sulphur formed is in a finely divided condition and is difficult to recover as such. Accordingly, the temperature is raised to a temperature above the melting temperature to agglomerate the elemental sulphur to liquid droplets. These liquid droplets are then solidified into pellets or pebbles by reducing the temperature below the melting temperature of sulphur. Cooling can be effected by any suitable means but preferably is accomplished by dilution with cool solution. Alternatively, the oxidation can be conducted at a temperature slightly above the melting point of the sulphur and the liquid droplets of sulphur so formed solidified by reducing the temperature below the melting point of sulphur. In either case, the temperature must be reduced below the melting point of sulphur before separation of solids from the liquid to solidify the sulphur pellets and thus facilitate handling at atmospheric pressure.

The total pressure at which the reaction is conducted is the pressure autogenously generated by the temperature plus the partial pressure of the free oxygen-bearing gas. The free oxygen-bearing gas can be oxygen, oxygen enriched air or air without oxygen enrichment. The most satisfactory results as regards velocity, extraction and the capital and operating costs of the apparatus employed are preferably obtained with a partial pressure of oxygen in the free oxygen-bearing gas of from above 25 pounds per square inch to 100 pounds per square inch. Pressures higher than 100

pounds per square inch can be employed but also are not economic because of inherent pumping difficulties and the necessary use of heavier, more costly pressure vessels. Higher pressures may be desired, however, when non-ferrous metals are present in the starting material.

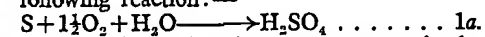
During oxidation, the slurry should be agitated to ensure a uniform dispersion necessary for maximum reaction with the free oxygen-bearing gas. Agitation also can be continued after oxidation to aid in coalescing elemental sulphur into droplets or pellets. The size of the liquid sulphur pellet is influenced by the extent and intensity of agitation as well as temperature. In general, the greater the intensity and extent of agitation and the higher the temperature up to 290° F., the larger are the liquid droplets of sulphur. During cooling agitation should be stopped to avoid breaking the sulphur pellets.

Elemental sulphur formed in the oxidation reaction is found in the undissolved residue from which it can be separated by screening or by other means. For example a mixture of solids in aqueous acidic sulphate solution withdrawn from the reaction vessel can be passed over a screen having openings of a size sufficient to retain the sulphur pellets while passing the solution and the undissolved residue. Alternatively, the mixture from the reaction vessel can be de-watered by suitable means, re-pulped in water, and the sulphur separated.

The method of the present invention is, of course, based on results obtained over a long period of research and investigations and is independent of hypothetical considerations. It is possible that the production of elemental sulphur and ferric oxide is the result of a reaction such as that expressed by the following equation:—

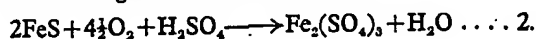


A part of the sulphur formed in this reaction is converted to sulphuric acid according to the following reaction:—



It is believed that the oxygen present in the gas phase diffuses through the gas—liquid interface into the liquid and in the liquid phase to the surfaces of the pulverulent pyrrhotitic material. Also, it is possible that sulphide ions diffuse in the solid pyrrhotitic particles to the surfaces where they are oxidized to elemental sulphur. Simultaneously, oxygen present on the surface may partially diffuse into the solid particles to oxidize ferrous iron to the ferric state.

During the course of the overall reaction 1, it is observed that small amounts of iron and sulphur are found in the solution as ferric sulphate. It is believed that this is caused by a side reaction as expressed in the following equation:—



This reaction is of a heterogenous nature in which gas, liquid and solid phase are involved.

The following examples illustrate the operation of the process in the treatment of pyrrhotitic mineral sulphides primarily for the production of elemental sulphur. These examples are illustrative only and are not intended to limit the scope of the invention.

The material treated in Examples 1 to 7 was

a pyrrhotite. On each example, the mixture of pulverulent pyrrhotitic mineral sulphides and aqueous sulphuric acid solution was agitated to maintain a relatively uniform suspension of particles and a maximum diffusion of free oxygen-bearing gas. The size of particles was about 100% minus 200 mesh Standard Tyler Screen.

TABLE I

| Example | Time (Hours) | Temp. (° F) | O ₂ Part. Press (psi) | Pulp Density % Solids | Sulphur Yield (%) |
|---------|--------------|-------------|----------------------------------|-----------------------|-------------------|
| 1 | ½ | 250 | 100 | 43—46 | 67.5 |
| 2 | 1 | 250 | 100 | 43—46 | 88 |
| 3 | 2 | 250 | 100 | 38 | 82 |
| 4 | 2 | 250 | 100 | 43—46 | 84 |
| 5 | 2 | 230 | 100 | 46 | 82.9 |
| 6 | 2 | 250 | 100 | 35 | 85.1 |
| 7 | 2 | 280 | 50 | 43—44 | 79.9 |

Table I illustrates that pyrrhotite dispersed in aqueous sulphuric acid solution to form a slurry comprised of 35% to 45% solids and heated for one to two hours at 230° F. to 250° F. and an oxygen partial pressure of about 100 pounds per square inch results in yields of elemental sulphur up to about 88% of the theoretical maximum yield. This sulphur was received in the form of pellets or pebbles

of 97% to 99% pure elemental sulphur.

The procedure of Examples 1 to 7 was repeated using a pyrrhotitic material having an analysis of 12.1% nickel, 1.45% copper and 28.2% sulphur.

The effect of adding sulphuric acid when using a pyrrhotitic starting material containing non-ferrous metals is shown by Example 8.

TABLE II

| Example | Time (Hours) | Temp. (° F.) | H ₂ SO ₄ Added | O ₂ Part. Press. (psi) | Sulphur Yield (%) |
|---------|--------------|--------------|--------------------------------------|-----------------------------------|-------------------|
| 8 | 2 | 230 | Yes | 185 | 73% |

Table II illustrates that addition of sulphuric acid increases the yield of sulphur in the low temperature oxidation treatment of the present method when treating pyrrhotitic material containing non-ferrous metals.

The method of the present invention also is ideally adapted for the treatment of pyrrhotitic mineral sulphides which contain non-ferrous metal values, and is particularly adapted for the treatment of pyrrhotitic mineral sulphides which are not readily amenable to concentration of the metal values by conventional concentrating processes, such as by flotation. That is, the pyrrhotitic material may be such that mineral particles are not exposed for attachment to the air bubbles in the flotation reaction or the desired minerals may be so finely disseminated throughout the ore that very fine grinding is necessary to release them with the result that the minerals form a slime rather than a pulp mixture amenable to flotation. Alternatively, the pyrrhotitic material may be a low grade middling product derived

from a previous flotation process and which contain minerals to the extent that a serious metal loss would result if they are discarded and yet which involve high capital and operating costs to extract and recover the metal values.

Regardless of the source of the sulphidic material, it has been found that it can be treated by the method of the present invention to produce a non-ferrous metal bearing product which is readily amenable to concentration by flotation.

In the treatment of pyrrhotitic mineral sulphides which contain non-ferrous metal values according to the method of the present invention and described in detail hereinbefore, pyrrhotitic material is first attacked by the oxidation treatment and elemental sulphur is formed. A portion of the non-ferrous mineral sulphides may be attacked under the strongly oxidizing conditions and enter the solution as soluble metal sulphates. However, at a temperature above the melting temperature of sul-

phur, the elemental sulphur tends to "wet" or enclose non-ferrous mineral sulphide particles as in a film, and thus protect them from further attack under the oxidizing conditions.

5 The resulting slurry is in ideal condition for treatment by a conventional flotation process for concentration of non-ferrous mineral sulphides and elemental sulphur, either with or without prior separation of the solution of sulphates from the solids.

10 Oxidation of sulphide sulphur of the pyrrhotitic material to elemental sulphur proceeds more rapidly than the oxidation of sulphide sulphur of the non-ferrous mineral sulphides. Thus, the time of retention and the oxygen partial pressure are determined with a view to obtaining the maximum oxidation of the sulphide sulphur in the pyrrhotitic material to elemental sulphur and separation
15 of non-ferrous mineral sulphides from the pyrrhotitic material.

The temperature at which the oxidation step is conducted, the time of retention and the partial pressure of oxygen are controlled to
25 obtain maximum oxidation of sulphide sulphur of the pyrrhotitic material to elemental sulphur having regard to the form in which it is desired to recover the non-ferrous metal values. That is, the method can be conducted
30 to obtain a maximum or minimum dissolution of non-ferrous metal values in the solution.

If it is desired to recover the major portion of the non-ferrous mineral sulphides occluded or enclosed in globules of elemental sulphur
35 with minimum dissolution of non-ferrous metal values in the aqueous acidified sulphate solution, the time of retention is controlled to obtain maximum oxidation of pyrrhotitic material and minimum oxidation of non-ferrous
40 mineral sulphides. For example, at a temperature of about 250° F. and at a partial pressure of oxygen of 100 pounds per square inch very satisfactory results are obtained with a time of retention of from 10 to 30 minutes.

45 It is found, also, that the treatment can be conducted with advantage at a temperature either below or above the melting temperature of sulphur. That is, from 230° F. to 250° F. If the treatment is conducted at a temperature below the melting temperature of sulphur, it is necessary to heat the slurry at the end of the oxidation period to a temperature above the melting temperature of sulphur with active agitation, thus to melt the sulphur and
55 agglomerate the particles into globules, after which the temperature is reduced to solidify the sulphur globules. Alternatively, the method can be conducted at a temperature above the melting temperature of sulphur, during which the
60 elemental sulphur is agglomerated into globules as it is formed and at the end of the oxidation period the temperature is reduced to solidify the sulphur globules into pellets. Oxidation at a temperature above the melting temperature of sulphur, for example, from 250°

F. to 290° F. favours the occlusion of non-ferrous mineral sulphides in the sulphur pellets. Oxidation at a temperature below the melting temperature of sulphur favours the oxidation of non-ferrous mineral sulphides to
70 sulphates. The rate of agitation should be reduced or stopped during cooling of the slurry to avoid breaking the sulphur pellets.

Elemental sulphur, the major portion of the iron values and sulphur-wetted mineral sulphides are found in the solid residue. Depending on the conditions under which the method is operated, some non-ferrous metal values and some of the iron may be extracted from the starting material and dissolved in the
75 aqueous acidified solution. The solids can be separated from the solution, such as by filtration. Elemental sulphur globules of greater than predetermined size, can, if desired, be separated from the solid residue such as by
85 screening, leaving a residue comprised mainly of iron oxide with lesser amounts of non-ferrous mineral sulphides included in the undersized elemental sulphur particles. This residue is in ideal condition for concentrating the non-ferrous mineral sulphides in a small fraction
90 of the original material.

A suitable method of collecting the sulphur and occluded non-ferrous mineral sulphides is a conventional oil-type flotation in acid circuit, pH2 to pH3.5, using 2.5 to 4 pounds of stove oil, kerosene, or fuel oil, with about 0.2 to 0.3 pounds of frother per ton of solids, dry weight. A further suitable flotation process is a conventional "sulphide" flotation process
100 at about atmospheric temperature using a sulphide collector such as a xanthate at pH7 to pH8.5, lime or soda ash being employed to neutralize the pulp, with a small amount of
105 frother.

As the mixture recovered from the oxidation treatment may have a pH value of about pH2, the oil-type flotation process is preferred in that it is not necessary to neutralize the pulp mixture prior to flotation.

The following examples illustrate the operation of the modification of the method of the present invention in the treatment of pyrrhotitic mineral sulphides which contain non-ferrous metal values:—
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FURTHER EXAMPLES

9. A pyrrhotitic middling material derived from the selective flotation of a nickel-copper bulk concentrate contained, after grinding and washing:—
120

| | |
|-----------------------|-------------------------|
| Iron—46.3% | Nickel—0.81% |
| Sulphur (Total) 30.5% | Sulphur elemental) 9.6% |

Sulphur (Sulphate) 1.0%
This material was slurried with dilute sulphuric acid solution, about 41% solids, and heated to a temperature of about 230° F. for a period of time varying from 0.5 to 2 hours with an oxygen partial pressure of about 100 pounds
125

per square inch. The temperature of the slurry was then raised to about 300° F. in the absence of oxygen for a period of about 15 minutes to agglomerate the sulphur into globules then cooled to below the melting temperature of sulphur to solidify the liquid sulphur globules into pebbles or pellets. The following results were obtained:—

| Time | % S recovered as elemental S | | % Ni recovered in solution |
|----------|------------------------------|---------|----------------------------|
| | pebbles | Residue | |
| 0.5 hrs. | 60.4% | 6.7% | 36.2% |
| 1.0 hrs. | 72.6% | 7.0% | 63.0% |
| 2 hrs. | 81.4% | 4.4% | 84.0% |

10. A pyrrhotitic material similar to 1 above was slurried with dilute sulphuric acid solution, pulp density about 46% solids, and reacted for two hours with an oxygen partial pressure of about 100 pounds per square inch with the following results:—

| Temp. | % S as elemental sulphur pebbles | | Ni in solution |
|---------|----------------------------------|---------|----------------|
| | + 48 mesh | Residue | |
| 230° F. | 72.8% | 10.1% | 69.5% |
| 250° F. | 73.3% | 8.7% | 78.3% |
| 280° F. | 40.7% | 8.2% | 21.8% |

11. Similar results are obtained in conducting the oxidation at a temperature slightly above the melting temperature of sulphur. The material treated was a low grade middling product obtained from a selective flotation process in which a high grade nickel sulphide concentrate was separated from a bulk concentrate containing both copper and nickel values. The middling product contained about 43.7% iron; about 1.73% nickel and about 28.5% sulphur. This material was ground for about one-half hour in a rod mill, slurried with dilute sulphuric acid solution, about 41% solids, and reacted at a temperature of about 250° F. under a partial pressure of oxygen of above 25 pounds per square inch.

It will be noted that under the described conditions of operation maximum non-ferrous metal extraction and dissolution in the aqueous solution is obtained at from 7 to 11 hours reaction time, whereas maximum recovery of such metal values as mineral sulphides in collectable form as such is obtained at from 1 to 3 hours, with the maximum total metal values and sulphur recovery being obtained in about 3 hours reaction time. The dissolution of non-ferrous metal values can be reduced by conducting the method at higher temperatures, of from 280° F. to 290° F., but the yield of elemental sulphur is reduced. The operating conditions are therefore determined with regard to the maximum extraction of non-ferrous mineral sulphides whether dissolved

in the aqueous solution or as sulphides and occluded in elemental sulphur particles and to the yield of elemental sulphur.

Following the separation of elemental sulphur from the flotation concentrate, a final concentrate was obtained which contained from 8% to 10% nickel, thereby effecting about a 6 to 1 concentration of non-ferrous metal values contained in material which otherwise was not amenable to treatment by a conventional flotation process.

The conditions under which the method is conducted are, of course, a matter of operating economics, having regard to the facilities available for treating the products of the method. For example, if the plant in which the method is operated has facilities for recovering metals from solutions, the method can be operated to obtain maximum yield of elemental sulphur and maximum conversion of non-ferrous metal values to and their dissolution in the leach solution as metal sulphates. It will be noted in this respect that in operating the method under the conditions prescribed above, 8.8% of the nickel values contained in the starting material entered the solution within the first hour and this extraction and dissolution increased to about 68.5% of the nickel as the time of retention was extended to eleven hours, and the grade of the concentrate was reduced accordingly.

However, if the plant in which the method is operated lacks facilities for recovering dissolved non-ferrous metal values from solutions, the method can be operated to obtain a maximum wetting of non-ferrous mineral sulphides by elemental sulphur with a minimum conversion of non-ferrous metal values to and their dissolution as soluble sulphates in the aqueous acid sulphate solution. It is found that this objective can be obtained by conducting the method at temperatures above the melting temperature of sulphur, for example, from 250° F. to 290° F., and by reducing the time of retention to from 11 hours to 3 hours. Under these conditions, it is found that about 25% of the nickel contained in the starting material is converted to and dissolved in the leach solution as a soluble sulphate and more than 65% of the nickel is collected as nickel sulphide by elemental sulphur and is readily amenable to concentration by a conventional flotation process such as described hereinabove.

As a further modification of the method, elemental sulphur can be added at the start of an operation to coat non-ferrous mineral sulphides and thus protect them against attack under the oxidising conditions. A portion of the elemental sulphur produced in each operation can be returned and mixed with the feed to the reaction zone to supply the elemental sulphur for this modification of the method.

Non-ferrous metal sulphates dissolved in the aqueous solution can be recovered, such as by treating the solution at elevated tem-

perature and pressure with a reducing gas such as carbon monoxide or hydrogen. Alternatively, if the plant in which the method is operated does not have facilities for recovering product metal from such solutions, non-ferrous metal values can be precipitated as sulphides, such as by one or other of the following methods, and added to the non-ferrous mineral sulphide concentrate for shipment to a metals recovery plant. For example, the aqueous solution can be neutralized, such as by calcium oxide, and then treated with a sulphide sulphur compound such as hydrogen sulphide or calcium sulphide to precipitate the non-ferrous metal values as sulphides.

Alternatively, non-ferrous metal values dissolved in the solution can be precipitated as sulphides by the addition of iron sulphide at elevated temperature, for example, from 300° F. to 400° F., according to the equation:—

$$\text{MeSO}_4 + \text{FeS} \longrightarrow \text{MeS} + \text{FeSO}_4$$
 in which "Me" is a non-ferrous metal.

The aqueous solution from the low temperature acid oxidation treatment can be treated for the precipitation and recovery of dissolved non-ferrous metal values and thereafter discarded or it can be re-cycled to the oxidation stage for re-use. Alternatively, a portion of the solution from the oxidation stage can be withdrawn from the re-cycled solution and treated such as described above or by crystallization of metal sulphates from the precipitation and recovery of non-ferrous metal values. This latter modification has the advantage that the solution can be maintained very easily and within predetermined non-ferrous metal values and the method conducted on a continuous basis.

The method of the present invention possesses a number of important advantages. Primarily, the method is directed to the treatment of pyrrhotitic sulphides for the production of elemental sulphur. However, the method possesses the important advantage in that it is ideally adapted for the treatment of pyrrhotitic mineral sulphides which is associated with non-ferrous mineral sulphides, including precious and noble metal values. The oxidation step is conducted under relatively low temperature and pressure conditions which permit the use of readily available conventional equipment. The reaction proceeds rapidly and is controlled readily to obtain maximum production of elemental sulphur of high purity. If non-ferrous metal values are present in the starting material, the oxidation step can be controlled to obtain either maximum dissolution of non-ferrous metal values in the aqueous solution or maximum occlusion of non-ferrous metal values in elemental sulphur particles with concurrent production of elemental sulphur. The method possesses the further important advantage in that it is ideally adapted for the treatment of pyrrhotitic material which contains non-ferrous metal

values which normally are not readily amenable to conventional concentration processes to prepare such metal values in a form in which they can be recovered inexpensively by conventional processes.

What we claim is:—

1. The method of producing elemental sulphur from pyrrhotitic mineral sulphides which comprises the steps of reacting pyrrhotitic mineral sulphides particles dispersed in an aqueous acidified sulphate solution (as hereinbefore defined) or in water containing a small amount of sulphuric acid at a temperature within the range of from 100° F. to 290° F. with a free oxygen bearing gas under a partial pressure of free oxygen above 25 pounds per square inch, continuing the reaction to oxidise sulphide sulphur contained in the pyrrhotitic material to elemental sulphur, agglomerating the elemental sulphur to liquid sulphur globules, cooling the liquid sulphur globules to below the melting temperature of sulphur to form elemental sulphur pellets, and recovering elemental sulphur pellets from the reaction mixture.

2. The method of treating pyrrhotitic mineral sulphides according to Claim 1 in which the mineral sulphides are associated with non-ferrous metal values characterised in that the oxidation reaction treatment is continued for a time period sufficient to occlude non-ferrous mineral sulphides in the elemental sulphur pellets and elemental sulphur and non-ferrous mineral sulphides are separately recovered from the recovered elemental sulphur pellets.

3. The method of treating pyrrhotitic mineral sulphides according to Claim 1 or Claim 2 characterised in that the oxidation reaction is conducted as a temperature below the melting temperature of sulphur, the reaction mixture is heated after the oxidation reaction to a temperature above the melting temperature of sulphur to agglomerate the sulphur to liquid globules.

4. The method of treating pyrrhotitic mineral sulphides according to Claim 1 or Claim 2 characterised in that the oxidation reaction is conducted at a temperature above the melting temperature of sulphur and is continued until the elemental sulphur is agglomerated as liquid globules.

5. The method of treating pyrrhotitic mineral sulphides according to any of the preceding claims characterised in that the size of the particles dispersed in the aqueous solution or acidified water is within the range of from 35 to 325 mesh Standard Tyler screen.

6. The method of treating pyrrhotitic mineral sulphides according to any of the preceding claims characterised in that the dispersion mixture in the oxidation reaction contains from 35% to 45%, by weight, solids.

7. The method of treating pyrrhotitic mineral sulphides according to any of the pre-

ceding claims characterised in that the oxidation reaction is conducted at a temperature within the range of from 200° F. to 290° F.

8. The method of treating pyrrhotitic mineral sulphides according to any of the preceding claims characterised in that the oxidation reaction is conducted under a partial pressure of free oxygen within the range of from above 25 to 100 pounds per square inch.

9. The method of treating pyrrhotitic mineral sulphides substantially as described.

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